

0.1 Direct observation of the effect of isotope-induced-disorder on exciton binding energy in $\text{LiH}_x\text{D}_{1-x}$ mixed crystals.

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Abstract. The results of the quantitative study of the renormalization of binding energy the Wannier - Mott exciton by the isotope effect are present for the first time. For this purpose accurate measurements of the intrinsic luminescence and mirror reflection spectra of $\text{LiH}_x\text{D}_{1-x}$ mixed crystals with a clean surface in the temperature range 2 - 100 K were carried. Nonlinear dependence of exciton binding energy E_b on the isotope mass $E_b \sim f(x)$ is caused by the bands fluctuation broadening which is connected with the isotope-induced-disorder. Temperature dependence of exciton binding energy is briefly discussed. The extrapolation of the asymptotic linear behavior of the exciton maximum energy to $T = 0$ K enables to estimate the zero - point renormalization of the exciton binding energy.

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A wide variety of novel isotope effects have been discovered on last four decades [1-6] owing to the availability of high-quality bulk semiconductor and insulator crystals with controlled isotopic composition (see, also, reviews [7-10]). Recent high resolution spectroscopic studies of excitonic and impurity transitions in high-quality samples of isotopically enriched Si have discovered the broadening bound excitons emission (absorption) lines connected with isotope-induced-disorder as well as the dependence of their binding energy on the isotope mass [11-13]. The last effect was early observed on the bound excitons in diamond [14-15] and more earlier on the free excitons in $\text{LiH}_x\text{D}_{1-x}$ mixed crystals [16].

As is well-known (see, for example [16, 17, 4]) the band gap energy E_g in the $T \rightarrow 0$ limit has a dependence on the average isotopic mass \overline{M} due to two effects: a) the renormalization of E_g by the electron-phonon interaction coupled with the dependence of the zero-point amplitudes on \overline{M} (see, also [18]) and b) the dependence of the lattice constant on \overline{M} , leading to a change in E_g through the hydrostatic deformation potential. The electron-phonon term is dominant [19, 20] and in the case of semiconductor crystals (C; Ge; Si) with a weak isotope scattering potential is varied approximately as $\overline{M}^{-1/2}$. The value of the $T = 0$ electron-phonon renormalization energy contribution to E_g can be independently determined from an extrapolation of the high temperature linear dependence

of $E_g \sim f(T)$ to $T=0$ but again it should be remembered that $E_g \sim f(T)$ also has a small contribution from change in volume with temperature. Therefore we should distinguish between effects of the average atomic mass (which imply the virtual crystal approximation - VCA) and effects of the mass fluctuations (randomness) superimposed onto the virtual crystal.

In this communication we report the first results of the quantitative study the dependence of free exciton's binding energy on isotope mass as well as on the temperature in $\text{LiH}_x\text{D}_{1-x}$ mixed crystals. We'll show that the exciton binding energy increase by 10 ± 1 meV from ${}^7\text{LiH}$ to ${}^7\text{LiD}$. Moreover, the dependence of $E_b \sim f(x)$ is nonlinear. The last effect, as will be shown below, is caused by the isotope-induced-disorder of $\text{LiH}_x\text{D}_{1-x}$ mixed crystals. Briefly part of these results have been published in [21].

Specimens of LiH , LiD $\text{LiH}_x\text{D}_{1-x}$ ($0 \leq x \leq 1$) as well as $\text{LiH}_x\text{F}_{1-x}$ were grown from melt using the modified Bridgman - Stockbarger method (see, also [22]). This technique is described many times early (see, e.g. [18, 2]). To improve the stoichiometric composition with respect to hydrogen (deuterium), the crystals grown were additionally annealed in an atmosphere of hydrogen or deuterium at a gas pressure of 3 to 5 atm. and a temperature 500 to 550°C (melting point is 961 and 964 K for LiH and LiD , respectively). For some crystals the time of heat treatment was as long as 20 days (for more details see [2,7]).

Given the high reactivity of freshly cleaved LiH crystals in the atmosphere, we had to develop a procedure of cleaving which would not only ensure an initially clean surface, but also allow us to keep it fresh for a few hours (the time taken to complete an experiment). These requirements are satisfied by the well-known method of cleaving directly in the helium chamber of the optical cryostat under liquid or superfluid helium, first tried in Ref. [23]. We did not notice any changes in the spectra of reflection or luminescence while working for 10 to 16 hours with surface prepared in this way. The device for cleaving the crystals had three degrees of freedom and rotated through 90° , which greatly helped in carrying out the experiments. As a rule, specimens for experiments were cleaved off bulk high - quality crystals. The experimental setup for measuring the low - temperature reflection and luminescence spectra has been described more than once (see, e.g. [7,18]) and consists of a double grating or prism monochromators, an immersion helium cryostat, and a photovoltaic detector (in photon counting mode). The results presented in this paper were obtained from a clean crystal surface cleaved, as described above, directly in the bath of helium cryostat. The spectra of mirror reflection were measured using an the angle of incidence of 45° . For our studies we selected specimens which exhibited low dependence of exciton spectra of reflection and luminescence on surface features.

As demonstrated earlier (see, e.g. [7]) most low-energy electron excitations in LiH (LiD) crystals are large-radius excitons. The spectrum of exciton photoluminescence of LiH crystals cleaved in liquid helium consists of a narrow (in the best crystals, its half-width is the $\Delta E \leq 10\text{meV}$) phononless emission line and its broader phonon repetitions, which arise due to radiative annihilation of excitons with the production of one to five longitudinal (LO) phonons (see, Fig. 1). The phononless emission line coincides in an almost resonant way with the

reflection line (see, insert Fig. 1) of the exciton ground state which is another indication of direct electron transition ($X_1 - X_4$ [2]). The lines of phonon replicas form an equidistant series biased toward lower energies from the resonance emission line of excitons. The energy difference between these lines is about 140 meV, which is close to the calculated energy of the LO phonon in the middle of the Brillouin zone [21] and measured in [19]. The isotopic shift of the zero-phonon emission line of LiH crystals equals that in reflection spectra, 103 meV (see, also, insert in Fig.1). As the deuterium concentrations increases, the width of the long-wave maximum in reflection (and the width of the phononless line in luminescence) spectra broadens and maximum shifts towards the shorter wavelengths. As can clearly see in Fig. 1, all spectra exhibit a similar long-wave structure. This circumstance allows us to attribute this structure to the excitation of the ground (1s) and the first excited (2s) exciton states [2]. Three effects are distinctly shown in the reflection spectra by an increase in deuterium concentration:

1. The shortwavelength shift of the reflection (as luminescence) spectrum as a whole;
2. The different velocity shift of the exciton maximum of the ground and the first excited states on the temperature (see, Fig. 2);
3. Broadening of the long-wavelength maximum due to excitation of the ground exciton state.

By the way we should note that the first excited exciton state is very clearly seen in the luminescence spectra too (see Fig. 3). Although two distinct contribution to ΔE_g (and respectively E_b) are present that due to the effect of the vibration on the lattice constant and the direct effect of the electron-phonon interaction [19, 20] for the present task of the dependence of the exciton binding energy on the isotope mass it will be considered only the mechanism of exciton-phonon interaction.

In accordance with the second effect in reflection spectra (see above point 2), as is to be expected, there is nonlinear dependence of the exciton binding energy ($E_b = 4/3\Delta_{12}$) on the isotope concentration. Displayed curve in Fig. 4 is the Wannier - Mott exciton binding energy value which are determined by the hydrogenlike expression $E_b = \frac{e^4\mu}{2\hbar^2\epsilon^2n^2}$ using for this E_1 and E_2 values from the reflection and luminescence spectra (see Figs. 1 and 3). The nonlinear nature of this dependence is similar to the theoretical results [25], where the influence of the chemical disorder of the crystal lattice on the Wannier - Mott exciton binding energy was seen and obtained a qualitative (not quantitative!) agreement with experimental results on the $\text{GaAs}_x\text{P}_{1-x}$ [26] mixed crystals.

Before the comparison of our experimental results with the theory developed by Elliott and Kanehisa [25], it would be prudent to briefly review main properties of their theoretical model. One of the principal result of paper [25] is the nonlinear dependence of exciton binding energy E_b on the concentration. As a consequence, the binding energy at half-and-half concentrations is less than the value derived from the crystal virtual model. According to Ref. [25] this model considers an exciton with a direct gap of a semiconductor alloy. Such a system

consists of an electron (particle 1) in the conduction band (c) with mass m_c and a hole (particle 2) in the valence band (v) with mass m_v . The problem of the exciton in disordered systems is to solve the Hamiltonian

$$H = \vec{p}^2/2m_c + \vec{p}^2/2m_v + u(\vec{r}_1 - \vec{r}_2) + V_c(\vec{r}_1) + V_v(\vec{r}_2), \quad (1)$$

with both the Coulomb interaction u and the potential V_v due to disorder ($\nu = c, v$). Reference [25] neglected disorder - induced interband mixing. As it is well known, in place of the electron-hole coordinates, (\vec{r}_1, \vec{p}_1) and (\vec{r}_2, \vec{p}_2) , one may introduce the center-of-mass and relative coordinates, (\vec{R}, \vec{P}) and (\vec{r}, \vec{p}) to rewrite (1) as

$$H = \vec{p}^2/2\mu_r + u(\vec{r}) + \vec{P}^2/2M + V_c(\vec{R} + m_v \vec{r}/M) + V_v(\vec{R} - m_c \vec{r}/M), \quad (2)$$

where μ_r and M are the reduced and total masses of excitons, respectively. Because of the random potential, the translational and relative degrees of freedom cannot be decoupled. This is essentially difficult when considering the two-body problem in a disordered system (see [25] and references therein). However, when the exciton state in question is well separated from other states so that the energy spacing is much larger than the translational width and disorder, one can forget about the relative motion ($H_r = \frac{\vec{p}^2}{2m_r} + u(\vec{r})$) and just apply any single-particle alloy theory solely to their translational motion. For each exciton state the translational part of Hamiltonian in this case is

$$H_t = \vec{P}^2/2M + \bar{V}_c(\vec{R}) + \bar{V}_v(\vec{R}) \quad (3).$$

Here \bar{V}_c and \bar{V}_v are averages of V_c and V_v with respect to the relative state ϕ , for example:

$$\bar{V}_c(\vec{R}) = \int d^3 \vec{r} |\phi(\vec{r})| 2V_c[\vec{R} + \frac{m_v}{M} \vec{r}] \quad (4).$$

This approach is very similar to the Born-Oppenheimer adiabatic approximation. Such situations hold in some mixed alkali halide crystals and probably A_2B_6 crystals. On the contrary, when the exciton binding energy is comparable to the disorder energy, the adiabatic approximation breaks down, and it is essential to take into account the effect of disorder on both the translational and relative motions. This is the case with the Wannier-Mott exciton in A_3B_5 alloys, for which the Elliott and Kanehisa model was developed. In this case the solution task is to start from the independent electron and hole by neglecting u in (2) and then to take into consideration the Coulomb interaction between the average electron and average hole. A further simplified approach adopted in the literature (see, for example [27] and references therein) in solving the Bethe-Salpeter equation [28] is to suppose a free-electron-like one particle Green's function with a built-in width to allow for the random potential due to disorder. In the cited theoretical model [25], the average (or "virtual crystal") gap is given by

$$E_g^{vc}(x) = E_0 + (\delta_c - \delta_v)(x - 1/2), \quad (5)$$

where E_0 is average gap, δ_c, δ_v are the values of the fluctuation broadening of the conduction and valence bands, respectively. Reference [25] also assumed the Hubbard density of states for both the conduction and valence bands with width W_c and W_v , respectively, as well as similar dispersion in both bands. With this

assumption the exciton binding energy has been calculated according to the coherent potential approximation CPA model. As is well-known, the main idea of the coherent potential methods in the introduction of an auxiliary medium with a regular, i.e., spatially periodic potential. By definition in the model this potential is also complex. The formalism of the coherent potential model, convenient for performing calculation and does not include fitting parameters, because of using of the density of phonon states from virtual crystal model which used virtual crystal approximation (VCA). It should be added here the key feature of the model developed in Ref. 25 is the short-range nature of the Coulomb potential (for details, see e.g. [7, 29]).

The data from Fig. 1 and other published sources [2, 7, 21] were used for plotting the energy E_b as a function of isotopic concentration x in Fig. 4. The binding energy (defined as the band edge minus the exciton energy) is given by [25]:

$$E_b^{crys} = U_0 + \frac{W}{2U_0} + W \quad (6).$$

In the last relation U_0 is the coupling constant at the total exciton momentum $\vec{q} = 0$.

Theoretical description of the binding energy of Wannier- Mott excitons as a function of concentration x was based on the polynomial derived by Elliott and coworkers [25]:

$$E_b = E_b^{crys} - E_{bow} \left[\frac{1-W}{2U_0} \right] - E_{eff}, \quad (7)$$

$$E_{eff} = x(1-x) \frac{\delta_c \delta_v}{W}, \quad (8)$$

where $W = W_c + W_v$, and W_c and W_v are the widths of the conduction band and the valence band which are equal to 21 eV [30] and 6 eV [31, 32] respectively. Here E_{bow} is the curvature parameter found from the function $E_g \propto f(x)$ ($E_{bow} = 0.046$ eV [7]); δ_c and δ_v are the magnitudes of the fluctuation smearing of the valence band and the conduction band edges, $\delta_c = 0.103$ eV and $\delta_v = -0.331$ eV. As follows from Fig. 4, these values of the parameters give a good enough description of the nonlinear dependence of the binding energy of Wannier-Mott exciton in disordered medium isotope - mixed crystals LiH_xD_{1-x} . This agreement between theory and experiment once again proves the inherent consistency of the model proposed by Kanehisa and Elliott, since the isotopic substitution affects the short-range part of the interaction potential.

In this way, the nonlinear dependence of the binding energy of Wannier-Mott exciton is caused by isotopic disordering of the crystal lattice. As is seen from Fig. 4 the exciton binding energy decreasing (relative linear law (VCA) - see dashed line in Fig. 4) in the vicinity of the middle meaning concentration really calls out the fluctuated broadening of the edge of the conduction and valence bands. In accordance with the theoretical model the last reason gives rise to the reduced E_g and there by the shallowing of the exciton levels and, respectively, the reduction of E_b .

As follows from Fig. 1, the addition of deuterium leads not only to the short-wave shift of the entire exciton structure (with different rates for 1s and 2s states), but also to a significant broadening of the long-wave exciton reflection line. This line is broadened 1.5 - 3-fold upon transition from pure LiH to

pure LiD. The measure of broadening was the halfwidth of the line measured in the standard way (see e.g. [33]) as the distance between the maximum and the minimum in the dispersion gap of the reflection spectrum, taken at half-height. The concentration dependence of the halfwidth (ΔE^R) of the long-wave band in the exciton reflection spectrum at 2 K is shown in Fig. 5. Despite the large spread and the very limited number of concentrations used, one immediately recognizes the nonlinear growth of ΔE^R with decreasing x . A similar concentration dependence of ΔE^R in the low-temperature reflection spectra of solid solutions of semiconductor compounds A_2B_6 and A_3B_5 has been reported more than once (see e.g. the review of Elliott and Ipatova [34] and references therein). The observed broadening of exciton lines is caused by the interaction of excitons with the potential of large-scale fluctuations in the composition of the solid solution. Efros and colleagues (see e.g. [35]) used the Lifshitz method of optimal fluctuation [36] to express the formula for the concentration dependence of the broadening of exciton reflection lines:

$$\Delta E^R = 0.5\alpha \left[\frac{x(1-x)}{Nr_{ex}} \right]^{1/2}. \quad (9)$$

where N - the concentration of sublattices nodes where the isotope substitutes are placed, $\alpha = dE_g/dx$; r_{ex} is the exciton radius which varies from 47 Å to 42 Å upon transition from LiH to LiD [2]. The results of calculation according to Eq. (9) are shown in Fig. 5 by a full curve.

The experimental results lie much closer to this curve than to the straight line plotted from the virtual crystal model. At the same time it is clear that there is only qualitative agreement between theory and experiment at $x > 0.5$. Nevertheless, even this qualitative analysis clearly points to the nonlinear dependence of broadening on the concentration of isotopes, and hence to the isotopic disordering. Since isotopic substitution only affects the energy of optical phonon for the first time, and, as a consequence, the constant of exciton-phonon interaction (in the first place, the Fröhlich interaction g_F^2), the nonlinearity of functions $\Delta E_b \propto f(x)$, $\Delta E^R \propto f(x)$ is mainly related to the nonlinear behavior of $g_F^2 \propto f(x)$. In this way, the experimental study of the concentration dependence of the exciton-phonon interaction constant may throw light on the nature and mechanism of the large-scale fluctuations of electron potential in isotopically disordered crystals.

Returning to the results of Fig. 2, let us add that the different temperature dependence of exciton peaks of $n = 1s$ and $2s$ exciton states leads to the temperature dependence of the binding energies of Wannier - Mott excitons

$$E_b \sim f(T) \quad (10).$$

This problem has not received any adequate treatment. More specifically, the energy of the exciton binding E_b in LiH crystals (as well as in mixed crystals LiH_xF_{1-x} (LiD_xF_{1-x})) decreases with increasing temperature, whereas E_b increases for excitons of the green and yellow series in Cu_2O crystals [34]. A linear approximation of the exciton binding energy in $LiD_{0.995}F_{0.005}$ (see curve 3, Fig. 2) representing E_b at $T=0$ K gives $E_b(0) \cong 55$ meV. From this value we can see that renormalization of the binding energy by the zero-point vibrations equals approximately $\simeq 10\%$ from this value, that is, on the other hand, com-

poses only half of renormalized exciton binding energy by isotope effect ($\simeq 10$ meV, see above). It is not excluded that the other part of renormalized exciton binding energy is caused by exciton-polar phonon interaction.

In conclusion, the exciton luminescence and reflection spectra are used in a quantitative study of the isotopic and temperature effects in $\text{LiH}_x\text{D}_{1-x}$ mixed crystals with a clean surface. It was shown that the short-range character of the potential of a disordered crystal lattice with isotope substitution is responsible for the broadening of the valence and conduction bands. Nonlinear dependence of the exciton binding energy on the isotope mass $E_b \sim f(x)$ is due the isotope-induced-disorder of $\text{LiH}_x\text{D}_{1-x}$ mixed crystals. Temperature dependence of exciton binding energy is briefly discussed. The extrapolation of the asymptotic linear behavior of the exciton maximum energy to $T = 0$ K enables to estimate the zero - point renormalization of the exciton binding energy.

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Figure captions.

1. Fig. 1. Luminescence spectra of free excitons at 2 K in LiH and LiD crystals cleaved in liquid helium. In insert: mirror reflection spectra of crystals. Curve 1: LiH; curve 2: $\text{LiH}_x\text{D}_{1-x}$ and curve 3: LiD. Curve 4 is the light source without crystals.

2. Fig. 2. Temperature dependence of the distance between the long-wavelength peaks (Δ_{12}) in specular reflection spectra of pure and mixed crystals: 1 - LiH; 2 - LiD; 3 - $\text{LiD}_{0.995}\text{F}_{0.005}$.

3. Fig. 3. The reflection (1) and luminescence (2) spectra of LiD crystal at 2 K.

4. Fig. 4. Concentration dependence of the binding energy of a Wannier - Mott exciton at 2 K in $\text{LiH}_x\text{D}_{1-x}$ mixed crystals: 1 - VCA approximation model; 2 - calculation according to equation (8); experimental points indicated by triangles.

5. Fig. 5. Concentration dependence of the half-width of the ground state line of the exciton in the mirror reflection spectrum at 2 K. 1 - VCA approximation model; 2 - calculation according to equation (9); experimental points are indicated by crosses.